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LUTETIUM YTTRIUM ORTHOSILICATE SINGLE CRYSTAL SCINTILLATOR DETECTOR

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LUTETIUM YTTRIUM ORTHOSILICATE SINGLE CRYSTAL SCINTILLATOR DETECTOR

This invention relates to a single crystal as scintillating detector for gamma ray or similar high energy radiation which single crystal is composed of Cerium doped Lutetium Yttrium orthosilicate (LYSO) with the general composition of $Ce_{2x}(Lu_{1-y}Y_y)_{2(1-x)}SiO_5$ where x = 0.0001 to 0.02 and y = 0.0001 to 1.9999 and claims priority based on U.S. Provisional Application Serial No.60/120,500 filed Feb. 18, 1999.

BACKGROUND AND PRIOR ART

There are a number of ways to detect high energy radiation. Some of the equipment can be quite bulky, such as a cloud chamber, others may not be as sensitive or quantitative. Scintillator is a very simple but also very accurate method to detect high energy radiation such as x-rays, gamma-rays, high energy particles exceeding a few kilo-electron-volts (KeV) in energy. When high energy radiation strikes on a scintillating crystal, it creates a large number of electron-hole pairs inside the crystal. Recombination of these electron-hole pairs will release energy in the range of a few eV. This energy can be emitted directly from the recombination center as light or transferred to a light emitting ion center which then emits a specific wavelength of light. This low energy emission can then be detected by a photomultiplier tube, avalanche photo diode (APD) or other detector systems with sufficient sensitivity. The higher the light emission (or light yield), the easier for the detector design.

The first scintillating crystal is calcium tungstate ($CaWO_4$) which was used before the turn of this century to detect x-rays. The most significant discovery of a scintillating crystal is Thallium-activated sodium iodide (NaI (Tl)) in the mid-40's. Even now, it is still the most widely used scintillating crystal. This is because large size crystals are readily available and quite inexpensive. Moreover, the light yield is the highest among all the known materials and

is still the benchmark standard for all other scintillator crystals even after all these years. Even though NaI(Tl) is widely used, it is not without problems. It is hygroscopic and very soft. Moreover, the density is too low (3.7 gm/cm3), the effective mass number (Z_{eef}) of 49 is also too small. It has a large and persistent after glow which interferes with the intensity counting system. Finally, the decay time about of 230 nanoseconds (ns) is too slow for many applications.

Since the turn of this century; there are a large number of crystals proposed for potential scintillating applications. Even though they do show scintillating properties, none of them has all the right properties. The common problems are low light yield, physical weakness and difficult to produce large size high quality single crystals. Despite the problems, a number of them have found applications in physics, chemistry, geology and medicine. One common feature of all these usable crystals is that they are the only crystals which can be produced in large size and high quality by industrial manufacturing process with reasonable cost. This has proven to be the most important factor than the details of scintillating properties to be considered as a viable scintillator material. The specific examples include bismuth germanate ((BGO) which is $Bi_4Ge_30_{12}$), cerium doped gadolinium orthosilicate ((GSO) which is Gd_2SiO_5) and cerium doped lutetium orthosilicate ((LSO) which is Lu_2SiO_5).

BGO was found in the early 70's. It has higher density (7.13 gm/cm^3) and is non-hygroscopic. But it also has problems such as low light yield (15% that of NaI(T1)), slow decay time (300 ns) and high refractive indices (n = 2.15) which results in light loss due to internal reflection. Still BGO scintillator crystals are now used in high energy calorimetry in particle physics research Institutes. It is also used as the detector for the 511 KeV gamma-ray radiation of the positron emission tomographs (PET) in medical imaging application. Because of the low light and slow decay, the image produced from the BGO PET machine tends to be

blurred with poor resolution.

In early 80's, the Ce doped GSO crystal was disclosed as a scintillator material. It has adequate density (6.71 gm/cm^3) and is also non-hygroscopic. The light yield is 20% of that obtained with NaI(Tl) with a much faster decay time (60 ns). Even though GSO crystals over 80 mm diameter have been produced, the crystal has not yet made in the PET market because of a strong cleavage plane. It is very difficult to cut and polishing the crystal into any specific shape without the risk of fracturing of the entire crystal. Another unexpected problem is the high thermal neutron capture cross-section (49,000 barns) of the gadolinium. It will interfere with the gamma rays generated by neutron irradiation source. However, since there is no neutron involved in the PET process, gadolinium containing GSO is not a problem.

In the late 80's, the Ce doped LSO crystal was disclosed as a good scintillator material. Similar to GSO, it has high density (7.4 gm/cm^3) and is non-hygroscopic. The light yield is significantly better and close to 75% that of NaI(T1) and the decay time is even faster (42 ns). The index of refraction is also very low (n = 1.82). Moreover, since LSO has a totally different crystal structure from GSO, it is fortuitous that in LSO structure, there is no any distinct cleavage plane making the material more suitable for detector block fabrication without the serious risk of fracturing. The thermal neutron capture cross-section is very low (84 barns) as compared to GSO. Lastly, it is now possible to commercially produce high quality, large size single crystals of LSO. Compared with all the other existing known scintillator crystals, Ce doped LSO seems to have the best combination of all the needed properties for PET or other high energy gamma-ray detector applications.

Unfortunately, the lutetium element of the crystal contains a trace amount of a natural long decay radioactive isotope, Lu^{176}, which will provide some background count rate that can be harmful for certain highly sensitive detector applications and the crystal has very deep trap

centers. This is evidenced by the very long phosphorescence after exposure to any UV light source. The light output measurement of a large number of LSO crystals shows an anti-correlation between trap-related integrated thermoluminescence output and scintillation light output over a range of several orders of magnitude. At present time, the crystal defect is the most serious issue. One can have two crystals with identical appearance with one having 100% light yield and the other failing to scintillate. Thus far, there is no understanding how these deep traps are formed in the first place and there is also no remedy how to reduce or eliminate them.

At present, the scintillation process has been well accepted and used in many applications. The basic mechanism is also reasonably well understood. It is generally accepted that the basic scintillation process involves three steps: (1) the absorption of the incident high energy radiation and the conversion into a large number of low energy (a few multiples of the band gap energy) electrons and hole pairs; (2) transfer the electron-hole recombination energy to the luminescence centers before its loss to multi-phonon relaxation processes; and, (3) the radiative emission of the transferred energy. In other word, the scintillation efficiency (E) can be expressed as:

$$E = \beta \times S \times Q$$

where β is the conversion efficiency, S is the transfer efficiency and Q is quantum efficiency of the radiation centers. Despite the understanding of scintillating mechanism based on the known materials, there is still lack of any good model which has the capability to predict the scintillating behavior of a specific compound. The quantum efficiency of an emission center can be predicted and tested optically; however, neither the total number of electron-hole pairs generated by an incident gamma ray radiation nor the transfer efficiency can be predicted or independently tested. In the end, the only way to confirm the scintillating behavior of a

compound is to make and then test it.

SUMMARY OF THE INVENTION

The first objective of the present invention is to provide a scintillation detector for use as a high-energy radiation detector.

The second objective of this invention is to provide an improved scintillation crystal for use as a gamma ray or other high energy radiation detector.

The third objective of this invention is to provide a monocrystalline scintillation crystal of improved performance for use as a gamma ray or other similar high energy radiation detector.

In the subject invention, an improved scintillation detector assembly has been realized comprising: a cerium doped lutetium yttrium orthosilicate crystal; and, a photodetector coupled to said crystal whereby an electrical signal is generated in response to a light pulse from said crystal when exposed a high energy gamma ray. The crystal is preferably monocrystalline and of a general composition of $Ce_{2x}(Lu_{1-y}Y_y)_{2(1-x)}SiO_5$ where x = 0.0001 to 0.02 and y = 0.0001 to 1.9999 whereby the detector utilizing said crystal as the scintillator responsive to gamma and other similar high energy radiation is particularly useful in the fields of physics, chemistry, medicine, geology and cosmology.

BRIEF DESCRIPTION OF THE FIGURES

Figs. 1a and 1b shows absorption and emission spectra of pure YSO and LSO.

Fig. 2 shows the LYSO scintillating light yield intensity as a function of lutetium concentration.

Fig. 3 shows the change of effective Z of LYSO as a function of lutetium concentration.

Fig. 4 is a pictoral representation of a typical cerium doped LYSO scintillating

detector.

DESCRIPTION OF REPRESENTATIVE EMBODIMENT

For illustrative purpose, a representative embodiment of the invention is described hereinafter in the context for the detection of high energy gamma rays. It will be understood that the LYSO single crystal scintillator of the invention is not limited to the detection of gamma ray radiation but it has the general application for the detection of other types of radiation such as x-rays, cosmic and other high energy particle rays.

In the background review, it is mentioned that Ce doped LSO has the best scintillating properties among all the known materials. But it still has a few serious problems to over come; namely, the isotope problem and the defect (deep trap) problem. In addition to these physical issues, LSO crystals also face two tough economic issues. First is the high melting temperature for growth. The melting point of LSO is estimated around 2200 C. It is among the highest melting temperature crystals produced commercially. Special high temperature ceramics were used to build the furnace and Iridium crucibles were used to contain the melt for growth. The growth process is quite detrimental to both insulation and the crucible. High cost of frequent replacement of the hardware pushes cost too high to be bearable for practical use. Second is the high cost of raw material of lutetium oxide. It is not a common material. Moreover, the current material purity around 99.99% is not sufficient to guarantee consistent high light yield. It is highly desirable to reduce or even replace lutetium oxide as the main ingredient in new scintillator crystals.

The embodiment of this invention is to design a new crystal which can eliminate most of the problems of LSO crystal without sacrifice the scintillating properties. Our initial motivation is to reduce the growth temperature of LSO single crystals. It is a very difficult task to maintain the operation at such high temperature for long period of time (> 1 week).

Since YSO has lower melting temperature near 2070 C, we are seeking the possibility to find an intermediate composition (or LYSO composition) which may melt at lower temperature to ease the growth process. We also want to minimize the yttrium content to retain the LSO scintillating properties.

Since there is no known published phase diagram between YSO and LSO, the phase relationship of the intermediate composition is not available. We speculate the melting and crystallization behavior of the intermediate LYSO crystal composition based on two assumptions. First, since both YSO and LSO have the same crystallographic structure and the ionic size of yttrium 3+ ion (0.090 nm) and lutetium 3+ ion (0.088 nm) are very similar, we assume that there is a 100% miscibility between the m'o compositions. In other word, it is possible to make any intermediate composition LYSO crystals without worry about phase separation or formation of new compounds. Second, since YSO has lower melting temperature, based on the model of ideal solid solution, it is expected that all the intermediate compositions will have lower melting temperature similar to the classic example of fosterite (Mg_2SiO_4) -fayalite (Fe_2SiO_4) pseudo-binary phase relations even though the exact position of the solidus and liquidus lines are not known.

In order to understand the melting and crystallization behavior, four intermediate LYSO charge compositions were prepared. The compositions were: $Ce_{0.002}(Lu_{0.7}Y_{0.3})_{1.998}Si_2O_5$ designated (70% LYSO); $Ce_{0.002}(Lu_{0.5}\ Y_{0.5})_{1.998}Si_2O_5$ designated (50% LYSO); $Ce_{0.002}(Lu_{0.3}\ Y_{0.7})_{1.998}Si_20_5$ designated (30% LYSO); and, $Ce_{0.002}(Lu_{0.15}Y_{0.85})_{1.998}Si_20_5$ designated as (15% LYSO). The percentage refers to the fraction of the lutetium in the crystal. A pure LSO charge was also prepared to be processes in similar way as a reference for direct comparison. To make sure that the property comparison is meaningful, all the LYSO crystal preparation procedures are identical. The same total number of moles of chemicals in each

case were used so that the finished crystals are near identical in size. To minimize the repetition, the 70% LYSO composition is hereafter set forth as the example to illustrate the preparation for all examples:

(1) A mixture of high purity fine powders consisting of 1,476 grams of Lu_2O_3, 359 grams of Y_2O_3, 317 grams of SiO_2 and 3.6 grams of CeO_2 were mechanically mixed thoroughly. The purity of Lu_2O_3 is 99.99%. The purity of both Y_2O_3 and SiO_2 is 99.9999.

(2) The mixed charge is placed in a 75 mm diameter by 75 mm deep iridium metal crucible and melted in a 50 kilowatt maximum power radio frequency (RF) heated high temperature furnace

(3) When the charge is fully molten and stabilized at near the melting temperature, a pure LSO seed crystal is lowered into the furnace and touched to the top center of the melt surface and the system is let to equilibrate.

(4) Once the seed is in equilibrium with the melt, the seed is pulled up slowly with rotation. A computer controlled automatic diameter controlled program is used to finish the growth to a crystal diameter of 30 mm while using a pull rate of 1.5 mm per hour.

(5) When the crystal has reached the desired length, it is separated from the melt and let cool slowly in the furnace to room temperature. The crystal is then recovered from the furnace and cut to smaller pieces for evaluation.

In order to check the melting behavior, an oversized crystal was grown in order to convert the maximum amount of melt to crystal. The resulting 30% LYSO crystal had a total length of 32 cm and a total weight of 1,880.5 grams. The crystal took 8 days to complete the growth. In this case, the bottom 5 cm portion of the crystal contains a lot of visual inclusions and defects and thus was not usable for evaluation. It did, however, provide important

information on the stability range of the melt.

Five crystals were grown consecutively in the same crucible and furnace at near identical growth conditions. There appeared to be no difference in crystal quality among all the five crystals. More interestingly, the fraction of the usable melt seems also to be quite the same regardless of the lutetium to yttrium ratio. This allows adjusting the crystal composition to best fit any specific application. In addition to the compositional flexibility, there was a significant lowering of the melting temperature which facilitates growth of these crystals.

To evaluate the scintillating properties, two 10 mm slabs were cut from each crystals, one from the top of the crystal and one from the bottom right above the defect region. It has been found that the scintillating light yield of any LSO crystal decreases systematically from the top to the bottom of the boule. The relative light yield can vary by as much as a factor of 2. It appears that this is due to the impurities in the lutetium oxide (Lu_20_3) source material. Since the LYSO also uses the same Lu_20_3 starting material, the LYSO will also show the same behavior.

The slab is placed under a Na^{22} radiation source which generates the 511 KeV gamma ray as the incident light. The scintillating light from the LYSO slab is captured by a Hamamatsu R877 photomultiplier. The scale used for the light output measurement is arbitrary unit. In this case, the light output for a standard NaI(Tl) scintillator is set at 100%. In comparison, the standard BGO crystal has a light output of 12.5%. The energy resolution is expressed as the full width at half maximum of the 511 KeV gamma ray peak. The result of the measurement is summarized in Table 1 and plotted in Fig. 2.

Table 1:

	YSO	15%LYSO	30%LYSO	50%LYSO	70%LYSO	LSO
Light yield %						
(top)	68	70	85	94	96	93
(bottom)	24	28	71	67	60	46
Energy Resolution %						
(top)	12	9	9	9	8	10
(bottom)	21	18	13	11	13	16
Effective Z	33	44	52	58	63	66
Density	4.62	5.04	5.45	6.01	6.57	7.4
Radiation length (cm)	9.5	4.5	2.3	1.6	1.2	1.1
Phosphore-scence	No	No	No	very weak	weak	Yes

First, the top portion of each crystal has the best scintillating value n since the crystallization process has been found to be a purification process. The first (top) portion The result has many important implications. of a crystal will have the least impurity content and thus the best performance. It is interesting to notice that the pure LSO crystal has produced light yield of 93% to that of NaI(T1). This is significant higher than the published result of 75%. This value may approach to the ultimate scintillating power for LSO.

Second, simply because of the top portion of each crystal has the highest purity, these measured values are good gauges for the comparison of the ultimate scintillating efficiency of these crystals. The light yield (or scintillating efficiency) remains constant for at least 50% percent substitution of lutetium with yttrium. Degradation of the light yield occurs after 70% replacement of lutetium. All the samples are of approximately equal thickness of 1 cm with no correction imposed for the reduction of density or effective Z. The scintillating efficiency drops rapidly with further addition of yttrium and the Compton signal rises rapidly with

more than 85% substitution. The simple conclusion can be drawn that LYSO is a valuable and very efficient scintillator as long as the crystal contains more than 30% lutetium.

Third, the result also shows the rapid reduction of the light yield as the growth is progressing and the greater fraction of the melt is converted to crystal. This is consistent with all the published speculation that impurities are the primary cause to create the deep trap, which gives the long phosphorescence and reduces the scintillating light yield. In the case of pure LSO, the light yield drops by a factor of 2 when 80% of the melt is converted to crystal. This is the largest drop as compared to all the other LYSO crystals.

In Fig. 2, it is shown that there is a linear reduction of light yield for the bottom portion of the LYSO and LSO crystals with linear increasing of lutetium content. This is the most direct evidence to show that the impurity is coming from the Lu_2O_3 starting material. The phosphorescence is greatly reduced with more yttrium substitution and is nearly unnoticed beyond 50% substitution.

In addition to the advantage directly observed from the light yield measurements, LYSO also resolves other problems associated with pure LSO. First, the growth temperature of LYSO is lower than that of pure LSO by approximately 100 C which is very significant in high temperature processes. Since the radiation heat loss is proportional to the 4^{th} power of temperature (or Tn) the high temperature insulation and iridium crucible will last longer. Second, substituting yttrium will reduce proportionally the trace concentration of the naturally radioactive Lu^{176} isotope without sacrificing the net light yield. This will, in effect, reduce the background noise of the detector. Third, both the cost and purity of the Lu_2O_3 starting material is a serious issue. Thus,Yttrium substitution will reduce the cost and improve the uniformity of scintillating efficiency for large single crystal plates. Further, since a low index of refraction is preferred for scintillating crystals to reduce the effect of

total internal reflection, the substitution of yttrium reduces the already low value of index of refraction of LSO.

Lastly, let us examine the issue of stopping power, radiation length and effective Z. For practicality, it is desirable to use material with highest Z and shortest radiation length. Interesting enough, we find that in the case of LYSO, the effective Z increases rapidly with small substitution of lutetium. It will eventually slow down when it approaching to 100% substitution. Fig. 3 illustrates such effect. As a consequence, 30% LYSO has the same effective Z as NaI(T1) and 60% LYSO has the same effective Z as GSO. In terms of the radiation length, we can save 30% lutetium with 10% increase of radiation length, save 50% and 70% lutetium with 1.5 and 2 times that of pure LSO. In other words, the reduction is not linear to the substitution. In fact, it is favor for the substitution.

Fig. 4 illustrates the structure of the scintillation device with the crystal of the invention optically connected to the photomultiplier or other photon detector.

While the invention has been described, disclosed, illustrated and shown in various terms of certain embodiments or modifications which it has presumed in practice, the scope of the invention is not intended to be, nor should it be deemed to be, limited thereby and such other modifications or embodiments as may be suggested by the teachings herein are particularly reserved especially as they fall within the breadth and scope of the claims here appended.